

**TITLE:** THE HOMOGENEOUS FORCING OF MERCURY  
OXIDATION TO PROVIDE LOW-COST CAPTURE

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## 1. ABSTRACT

### Objectives

Mercury that exits the furnace in the oxidized form ( $\text{HgCl}_2$ ), as opposed to elemental mercury, is known to be much more easily captured in existing pollution control equipment (*e.g.*, wet scrubbers for  $\text{SO}_2$ ). This is principally due to the high solubility of the oxidized form in water. Work over the last several years in our lab and elsewhere has identified the general outlines of how this oxidation occurs.

The scenario is as follows. In the flame the mercury is quantitatively vaporized as elemental mercury. Also, the chlorine in the fuel is released as  $\text{HCl}$ . The direct reaction  $\text{Hg} + \text{HCl}$  is well known to be far too slow to be of practical consequence in oxidation. The high temperature region does, however, generate a small concentration of atomic chlorine from the  $\text{HCl}$ . As the gases cool (either in the furnace convective passes, or within a sample probe), the decay in  $\text{Cl}$  atom is constrained by the slowness of the principal recombination reaction,  $\text{Cl} + \text{Cl} + \text{M} \rightarrow \text{Cl}_2 + \text{M}$ . This allows chlorine atom to hold a temporary, local superequilibrium concentration. Once the gases drop below about  $550^\circ\text{C}$ , the mercury equilibrium shifts to favor  $\text{HgCl}_2$  over  $\text{Hg}$ , and this superequilibrium chlorine atom promotes oxidation via the fast reactions

$\text{Hg} + \text{Cl} + \text{M} \rightarrow \text{HgCl} + \text{M}$  and  $\text{HgCl} + \text{Cl}_2 \rightarrow \text{HgCl}_2 + \text{Cl}$ . Thus, the high temperature region provides the Cl needed for the reaction, while the quench region allows the Cl to persist and oxidize the mercury in the absence of decomposition reactions that would destroy the  $\text{HgCl}_2$ .

While this mechanism is successful in explaining many of the observations seen in the laboratory, a critical question is how this understanding can be used to promote oxidation in an inexpensive way such that capture can be improved without adding new back end pollution control equipment. Under our Phase I grant, we investigated the use of additives to promote the oxidation. The idea was to use  $\text{H}_2$  or CO whose breakdown would yield free radicals that would promote Cl formation from HCl via reactions such as  $\text{OH} + \text{HCl} \rightarrow \text{Cl} + \text{H}_2\text{O}$ . The results indicated that each of these additives by themselves were less than optimally effective. For  $\text{H}_2$ , the reaction  $\text{H}_2 + \text{Cl} \rightarrow \text{HCl} + \text{H}$  tended to reduce atomic chlorine concentrations. There was no corresponding reaction for CO, but the high temperature required to initiate CO oxidation tended to place the reaction at a point where elemental Hg was the favored species. We found that a mixture of CO and  $\text{H}_2$  was much more effective. It appears that the  $\text{H}_2$  oxidation initiates CO oxidation at a lower temperature, leading to excess radical formation with reduced  $\text{H}_2$  concentrations. The present grant focuses on exploring and optimizing this observation.

### **Accomplishments to Date**

During the current period of performance we have used a flow reactor system to systematically explore the following variables: temperature, CO concentration,  $\text{H}_2$  concentration, and HCl concentration. The results to date indicate that the most sensitive variables are the injection temperature of the additives, and the ratio of CO/ $\text{H}_2$ . The optimum injection temperature appears to be around  $500^\circ\text{C}$  and the CO/ $\text{H}_2$  ratio is of the order of 5. Presently, we can increase oxidation from 20 to 50% at our best condition. We are continuing to fill in this experimental matrix.

### **Future Work**

We plan to finish filling in our experimental matrix. We also will work briefly with gas mixtures containing  $\text{SO}_2$  and/or NO as these have been noted by others as modifying Hg oxidation behavior. We will use a detailed chemical kinetic model, cast in plug flow form, to attempt a complete chemical interpretation of our data. An ultimate goal is to generate the CO/ $\text{H}_2$  mixture via a simple on-line reforming of natural gas at the plant site. As such, we will look briefly at the flexibility we can tolerate in CO/ $\text{H}_2$  ratios.

## **2. LIST OF PUBLISHED JOURNAL ARTICLES, COMPLETED PRESENTATIONS, AND STUDENTS RECEIVING SUPPORT FROM THE GRANT**

### **Conference Presentations**

- Study of the forced oxidation of mercury in post-combustion gases. L. Castiglione and J. Kramlich. Abstract-Pacific Northwest Regional Environmental Symposium, 2004, Submitted.

### **Students Supported Under this Grant**

- Linda Castiglione, Ph.D. student in the Department of Mechanical Engineering, University of Washington